Complex Triarylsulfonium Salt Photoinitiators. II. The Preparation of Several New Complex Triarylsulfonium Salts and the Influence of Their Structure in Photoinitiated Cationic Polymerization

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Synopsis

Complex triarylsulfonium salts bearing the thiophenoxy chromophore have been synthesized. The effects of the position of attachment of the thiophenoxy group on the rate of photolysis and in the photoinitiated cationic polymerization of various monomers have been investigated. Other salts in which the thiophenoxy group has been oxidized to the sulfoxide and the sulfone also were prepared to examine the effects of the oxidation state of the sulfur-bearing chromophore on the efficiencies in photoinitiated cationic polymerization. All complex salts having extended conjugation not impeded through positional isomerization or blocked through oxidation of the thiophenoxy chromophore are more reactive than the corresponding triphenylsulfonium salts in cationic polymerization.

INTRODUCTION

In Part I of this two-part series, we described the identification and characterization of diphenyl-4-thiophenoxyphenylsulfonium salts (I):

I
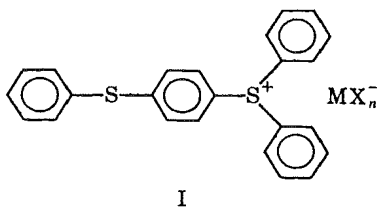
bearing non-nucleophilic anions of the type $MX_n^- = BF_4^-$, AsF_6^-, PF_6^-, and SbF_6^- as a new class of exceptionally efficient photoinitiators for cationic polymerization.[1] The greater photoefficiency of I compared to the corresponding triphenylsulfonium salts was attributed to the extended conjugation resulting from the presence of the 4-thiophenoxy chromophore in these compounds.

In view of the high photoefficiencies of I, it seemed worthwhile to prepare a number of structurally related and isomeric complex triarylsulfonium salts and to determine the effects of structure on their photochemistry and activity in cationic polymerization.

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EXPERIMENTAL

Starting Materials and Reagents

All reagents and starting materials used in the synthesis of the complex sulfonium salts were reagent grade and were used without purification. The synthesis of various diaryliodonium salts used in the preparation of complex triarylsulfonium salts has been described previously[3,4] as has the synthesis of triphenylsulfonium hexafluoroarsenate.[1,5] Cyclohexene oxide (7-oxabicyclo[4.1.0]heptane), 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate, 2-chloroethyl vinyl ether, β-pinene, and methylene chloride were dried over calcium hydride and then were purified by fractional distillation. s-Trioxane was freshly sublimed prior to use. All monomers were purified and then used immediately.

General Preparation of Complex Triarylsulfonium Salts III–VIII

To a 250-ml round-bottomed flask equipped with a condenser, Dean–Stark trap, and thermometer there were placed 19.6 g (0.35 mole) of 86% KOH, 33 g (0.3 mole) of thiophenol, and 120 ml of dimethylacetamide. The mixture was heated at 150°C, and 6.5 ml of water was collected. To the potassium thiophenoxide solution there was added 26.3 g (0.11 mole) of o-, m-, or p-dibromobenzene and the reaction mixture was heated at reflux for 6 hr. After cooling, the reaction mixture was added to 300 ml of water and the precipitated dithiophenoxy benzene was collected by filtration, washed with water, and air-dried overnight.

The dithiophenoxybenzenes were arylated by combining 7.35 g (0.025 mole) of the disulfides, 0.2 g of copper benzoate, and 0.025 mole of the desired diphenyl, di-4-t-butylphenyl, or di-3,4-dimethylphenyl iodonium salt in a 50-ml round-bottomed flask equipped with a magnetic stirrer and condenser and by heating in an oil bath. The usual conditions of 3 hr at 120–130°C were used for all the salts with the exception of VI which required 5.5 hr at 180°C for successful arylation to take place. On cooling, the brown reaction mixtures were washed several times with 50-ml portions of diethyl ether to remove iodobenzene, and the remaining impure salts were recrystallized from 95% ethanol to yield the pure complex triarylsulfonium salts.

Oxidation of Diphenyl-4-Thiophenoxyphenylsulfonium Hexafluoroarsenate III

Preparation of Sulfone X

Into a 125-ml Erlenmeyer flask were placed 11.2 g (0.02 mole) of sulfonium salt III and 20 ml of glacial acetic acid. To this suspension was added (with stirring and cooling) 4 ml of 30% hydrogen peroxide. When the addition was complete, stirring was maintained overnight (16 hr) at room temperature. During the reaction, the mixture changed from a suspension to a cloudy solution. The reaction mixture was poured into 100 ml of water and a semisolid gray material was obtained. After washing twice with water and once with diethyl ether, the product was dried for 16 hr at 25°C in vacuo. The yield of isolated sulfone X (mp 65–75°C) was 8.5 g or 72% theoretical.

The infrared (IR) spectrum (KBr disk) shows bands at 1330, 1160 (s); 1050–1100, 830 (w); and 750 cm^{-1} (s), which compare favorably to the literature assignments for the analogous perchlorate salt.[6]

Preparation of Sulfoxide IX

To 11.2 g (0.02 mole) of sulfonium salt III suspended in 15 ml of acetone, 2 ml of 30% hydrogen peroxide was slowly added with cooling. The reaction was stirred overnight at room temperature and the light brown solution was poured into 100 ml of water. The oil was separated by decantation and was washed twice with water and then with anhydrous diethyl ether. The product which had solidified during the washings was dried at 60°C for 16 hr in a vacuum oven. A 9.1-g yield (79% theoretical) of the pure sulfoxide IX was obtained (mp 70–74°C) having a strong S—O absorption band at 1065 cm^{-1} in the IR.

Photolysis Studies

Photolyses were conducted with a Hanovia 450-W medium-pressure mercury arc lamp with a measured output of 13,000 μW/cm^2 from 200 to 300 nm at a distance of 5 cm. Surrounding the lamp was a quartz well through which cooling water was pumped. Sample tubes were placed in a merry-go-round holder that was rotated continuously with a motor to provide even illumination throughout the photolysis. The entire apparatus was placed in a large thermostatted water bath which controlled the temperature within 1°C.
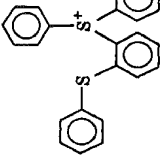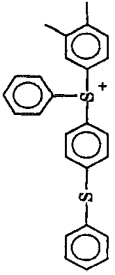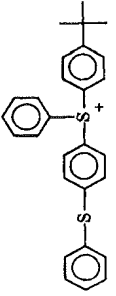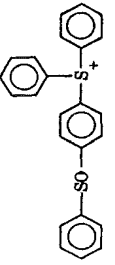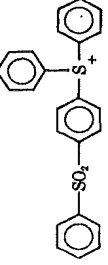
Photodecomposition Studies

The photodecomposition of triarylsulfonium salts was carried out by irradiating 0.07M solutions of the salts in acetonitrile in quartz sample tubes. The photolysis products were identified by a combination of two analytical techniques. The products initially were identified by a comparison of their high-pressure liquid chromatography (HPLC) retention times with the retention times obtained from authentic samples. Confirmation of the structural assignment was then made with a gas–liquid chromatograph (GLC)–mass spectrometer. Once the products were identified by these two methods, their concentrations were routinely determined by GLC.

Photopolymerizations

Stock solutions were prepared by dissolving the sulfonium salt photoinitiator in the bulk monomer in the case of cyclohexene oxide or in a mixture of methylene chloride and 2-chloroethyl vinyl ether, s-trioxane, or β-pinene. Five-milliliter aliquots of the stock solutions were sealed under nitrogen into vials fitted with polyethylene-lined caps. Photopolymerizations were conducted by placing the vials in the merry-go-round apparatus and irradiating them with a 450-W Hanovia lamp. All photopolymerizations were conducted at 25°C. The samples

TABLE I
Structure and Properties of Complex Triarylsulfonium Salts

Compound	Cation	Anion	mp (°C)	λ_{max} (ϵ)	Elemental analysis			Yield (%)
					C (%)	H (%)	S (%)	
II		AsF$_6^-$	195–197	227(21,000)	Calcd: 47.68 / Found: 47.78	3.31 / 3.41	7.06 / 7.06	40
III		AsF$_6^-$	76–77	225(23,400) 300(19,500)	Calcd: 51.43 / Found: 51.21	3.40 / 3.59	11.43 / 11.37	45
IV		PF$_6^-$	79–83	227(22,240) 300(18,020)	Calcd: 55.81 / Found: 55.87	12.40 / 12.62	3.68 / 3.89	55
V		AsF$_6^-$	Oil	230(24,330)	Calcd: 51.43 / Found: 51.14	3.39 / 3.43	11.43 / 11.43	35.7

Compound	Structure	Anion	mp (°C)	λ nm (ε)	Analysis	C	H	As	Yield (%)
VI		AsF_6^-	148–158	230(25,250)	Calcd: Found:	51.43 51.32	3.39 3.44	11.43 11.66	18
VII		AsF_6^-	Oil	235(21,600) 300(19,660)	Calcd: Found:	53.06 53.28	3.91 4.06	10.88 10.68	32
VIII		AsF_6^-	Oil	230(23,300) 300(19,660)	Calcd: Found:	54.55 55.39	4.38 4.26	10.39 10.15	52
IX		AsF_6^-	70–75	230(22,300) 300(19,300)	Calcd: Found:	50.00 49.87	3.23 3.06	11.11 11.35	79
X		AsF_6^-	64–65	243(25,200)	Calcd: Found:	48.65 48.81	3.21 3.49	10.81 11.07	72

were quenched at various irradiation times by adding 1 ml of a methanolic solution that contained a small amount of NH_4OH into the reaction mixtures and then pouring the solutions into methanol. After filtering the coagulated polymers and washing them with methanol, they were dried at 60°C *in vacuo* and were weighed.

Differential Scanning Calorimetric Determination of Dye Sensitization

An apparatus essentially identical with that described by Moore et al.[7] was used in these studies. A Perkin–Elmer DSC II thermal analyzer equipped with a differential scanning calorimeter (DSC) module and modified with a cylindrical quartz cell enclosure and window, a GE H3T7 medium-pressure mercury arc lamp, a shutter, and a transmission filter system was used in these studies. The apparatus was fitted with a glass transmission filter that permitted passage of wavelengths only greater than 390 nm. Approximately 10-mg samples of 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate containing 3% by
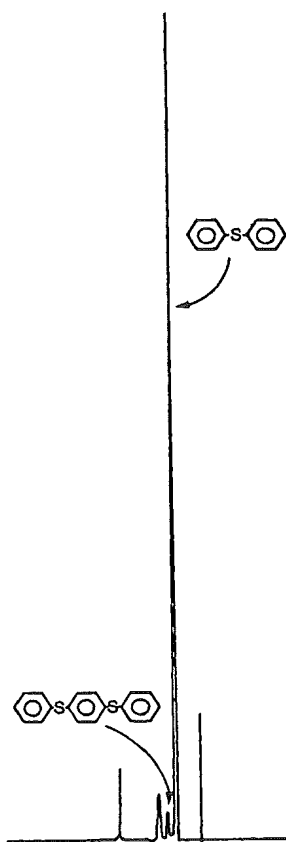

Fig. 1. HPLC analysis of the photolysis of III (column: micro-Bondapak, CN; solvent: THF, isooctane; chart speed: 0.1 in./min).
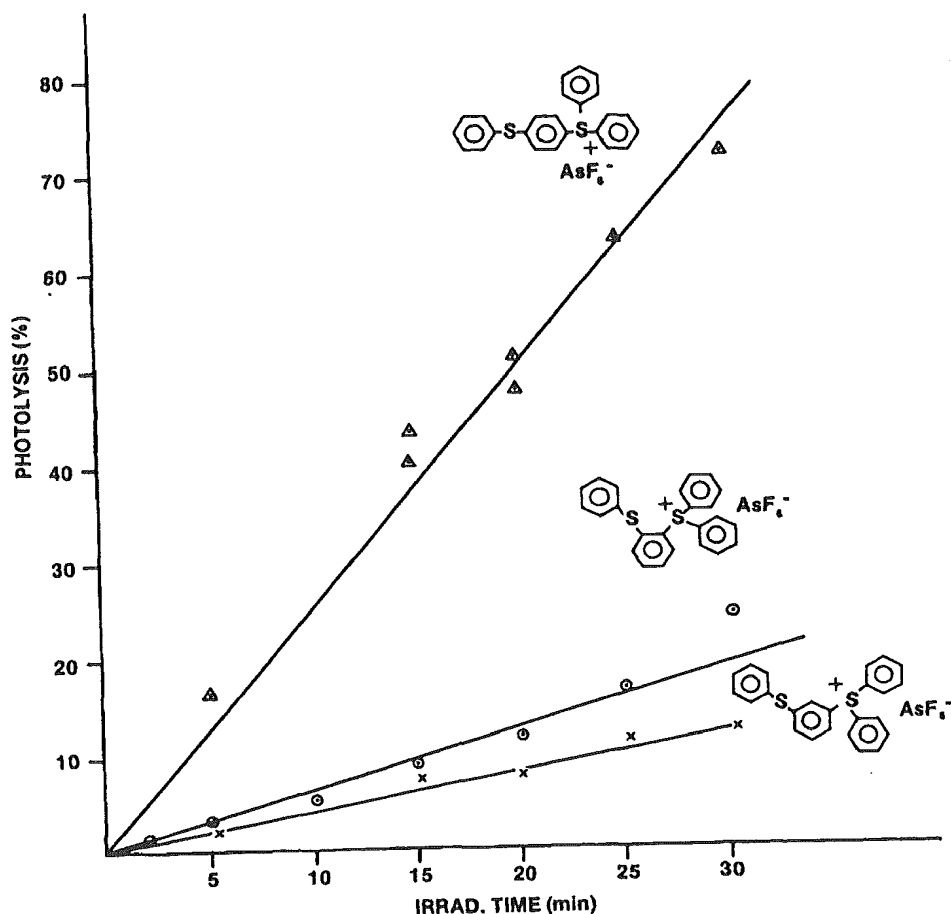
Fig. 2. Comparison of the photolysis rates of different isomeric diphenyl thiophenoxyphenyl-sulfonium salts ($0.07M$ in acetonitrile).

weight of complex triarylsulfonium salt III and 0.5% of the perylene were placed in aluminum sample cups. The samples were irradiated in the DSC apparatus in an isothermal mode at 25°C.

RESULTS AND DISCUSSION

Synthesis of Complex Triarylsulfonium Salt Photoinitiators

The eight complex triarylsulfonium salt photoinitiators shown in Table I were prepared to investigate the effects of structure and positional isomerism on their photolysis and activity in photoinduced cationic polymerization. Triphenyl-sulfonium hexafluoroarsenate (II), whose synthesis has been described previously,[1,2] was included in the table for purposes of comparison. The copper-
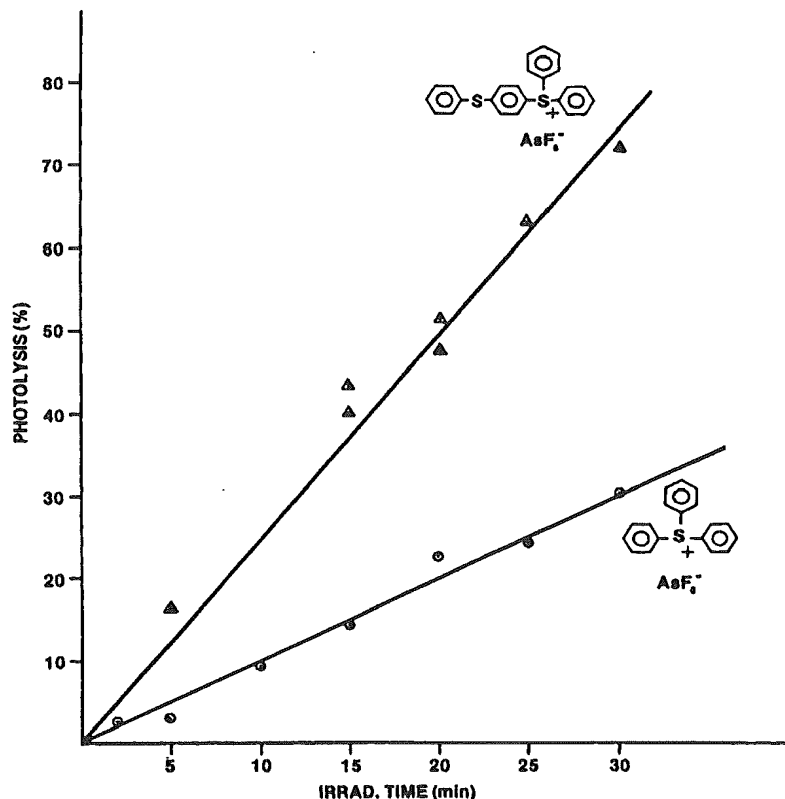
Fig. 3. Comparison of the photolysis rates of triphenylsulfonium and diphenyl-4-thiophenoxy-phenylsulfonium salts (0.07M in acetonitrile).

catalyzed arylation of diarylsulfides with diaryliodonium salts developed in the laboratory was used extensively in the preparation of these compounds.[2]

In eq. (1) is shown the general scheme used in the syntheses of compounds III–VIII.
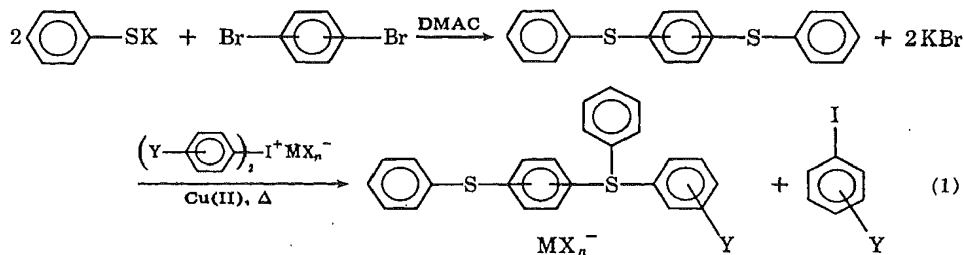
The three isomeric salts—III, V, and VI—were prepared to examine the effects of the site of attachment of the thiophenoxy substituent. Although the ortho-substituted compound VI at first appeared to present considerable synthetic difficulties resulting from severe steric crowding in the molecule, space-filling molecular models indicated that the compound could be made. In fact, good

yields of VI could be obtained by carrying out the arylation reaction under the somewhat more severe conditions of 180°C for 5.5 hr instead of the usual 125–130°C for 3 hr.

The sulfoxide IX and the sulfone X were prepared by oxidation of the parent sulfonium salt III as shown in eq. (2).

$$\text{(2)}$$
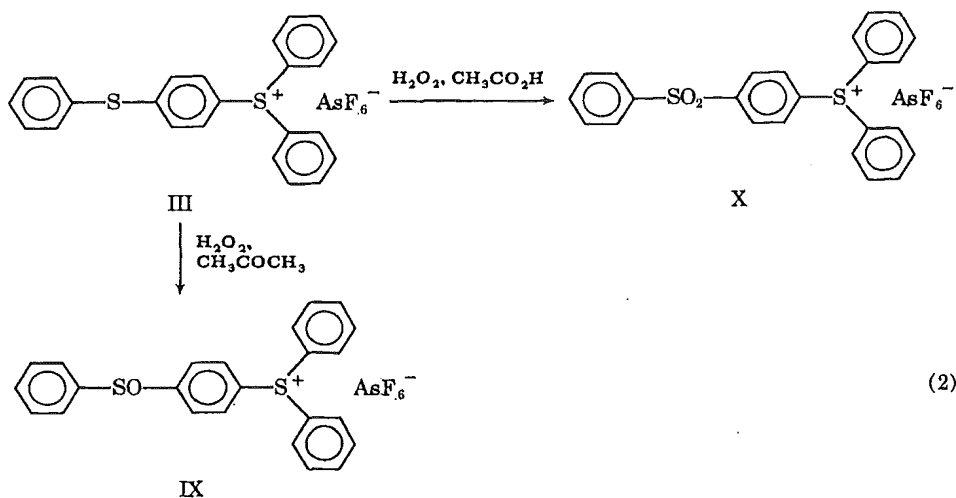
Photolysis of Complex Triarylsulfonium Salts

Photolysis of the three isomeric triarylsulfonium salts—III, V, and VI—as 0.07M solutions in acetonitrile was conducted in quartz ampules using a Hanovia 450-W mercury arc lamp. The samples were irradiated for 10 min or to approximately 20% conversion to avoid the formation of secondary photolysis products. Identification of the photolysis products by HPLC was made by comparison with the retention times of authentic samples. Figure 1 shows the HPLC trace of the product mixture derived from the photolysis of III which is typical of these three compounds. The major product of the photolysis (>95%) is diphenylsulfide with only a trace of 1,4-dithiophenoxybenzene present. Photoinduced cleavage, therefore, does not occur randomly in III, V, and VI but specifically at one carbon–sulfur bond as shown in eq. (3).

$$\text{(3)}$$
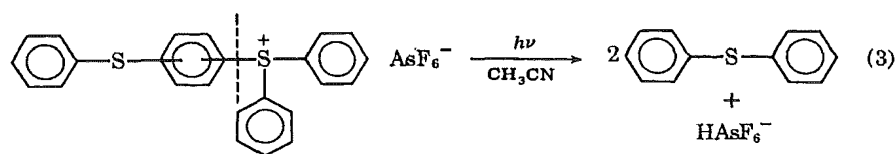
Accordingly, we have used a gas–liquid chromatography (GLC) analysis for diphenylsulfide as a rapid method of determining the photolysis rates of III, V, and VI. The curves in Figure 2 give a direct comparison of the rates of photolysis of these salts. As expected, the resonance effect of the thiophenoxy group is at
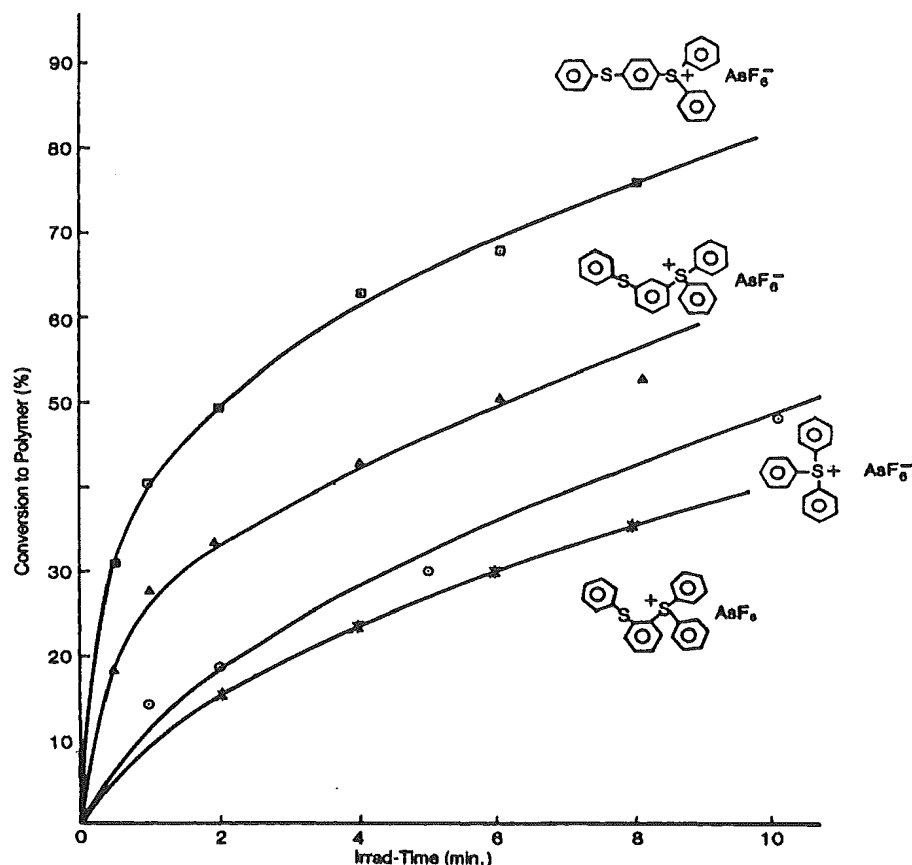
Fig. 4. Photopolymerization of cyclohexene oxide at 20°C using 0.021M different sulfonium salt photoinitiators.

its greatest in the para-substituted compound, III, giving the highest photolysis rates. In the ortho compound, VI, the steric constraints of the molecule would be expected to impede resonance interaction of the sulfur lone electron pairs by torsionally rotating the aromatic rings thereby minimizing overlap with the adjacent aromatic rings. Finally, in the meta compound, V, resonance interaction of the thiophenoxy group is minimized by its position with respect to the positively charged sulfur atom.

It is also instructive to compare the relative rates of photolysis of triphenylsulfonium hexafluoroarsenate (II) with the diphenyl-4-thiophenoxyphenylsulfonium analog (III). As is shown in the two curves in Figure 3, the rate of photolysis of the latter compound is substantially higher than that of the former. Because of the presence of the broad band at 300–303 nm, which substantially overlaps with the major mercury emission band at 313 nm, salt III is capable of capturing more of the light emitted by the irradiation source than the simple triphenylsulfonium salt II in which this band is missing.

The sulfoxide IX and sulfone X were photolyzed and the products of photolysis were elucidated by HPLC. Irradiation of these compounds leads in both cases
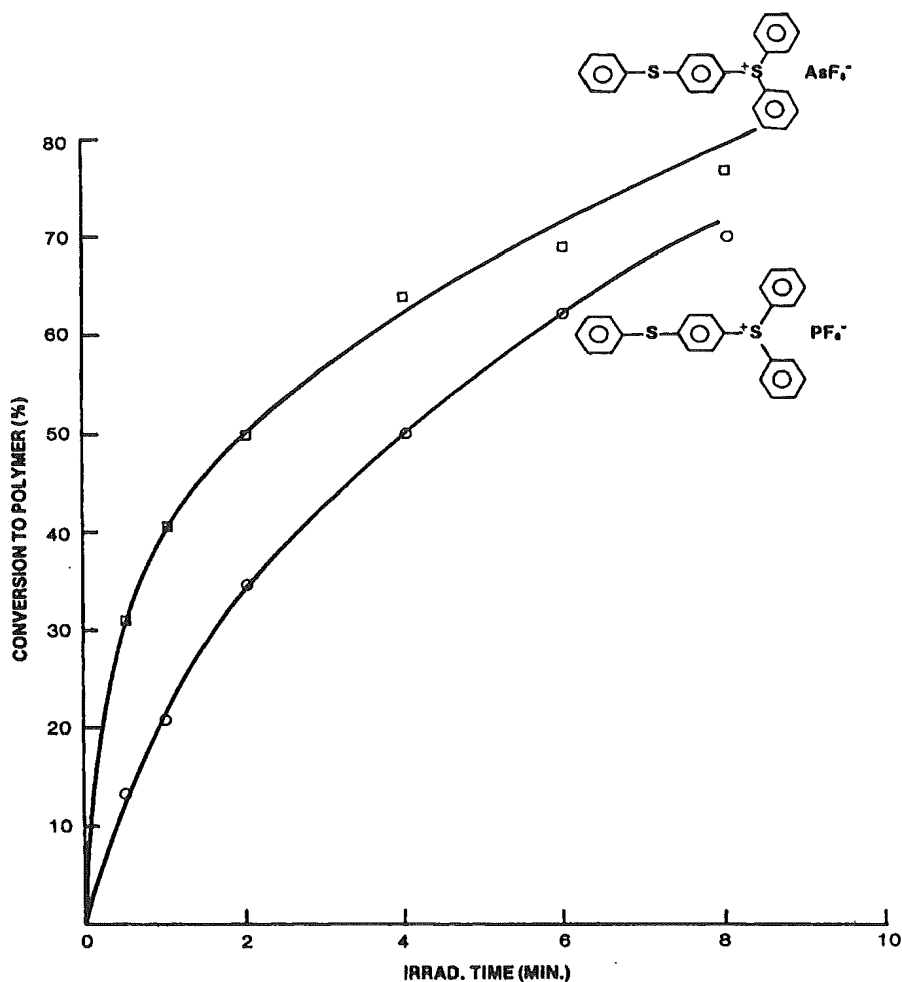
Fig. 5. Comparison of complex sulfonium salts III and IV in the bulk photopolymerization of cyclohexene oxide at 20°C (photoinitiator concentration = 3 mole %).

to the formation of diphenylsulfide as the major product. In addition, IX and X give, respectively, diphenylsulfoxide and diphenylsulfone, and in neither case was the presence of benzene detected. These results also are consistent with specific cleavage in these two compounds at the same carbon–sulfur bond as was shown in eq. (3) for compounds III, V, and VI.

Photoinitiated Cationic Polymerization Using Complex Triarylsulfonium Salts

On the basis of the observed differences in the structurally dependent photolysis rates of these complex triarylsulfonium salts, one would predict substantial differences in their efficiencies in the photoinitiation of cationic polymerization. Figure 4 gives a comparison of all three isomeric diphenyl thiophenoxyphenyl-
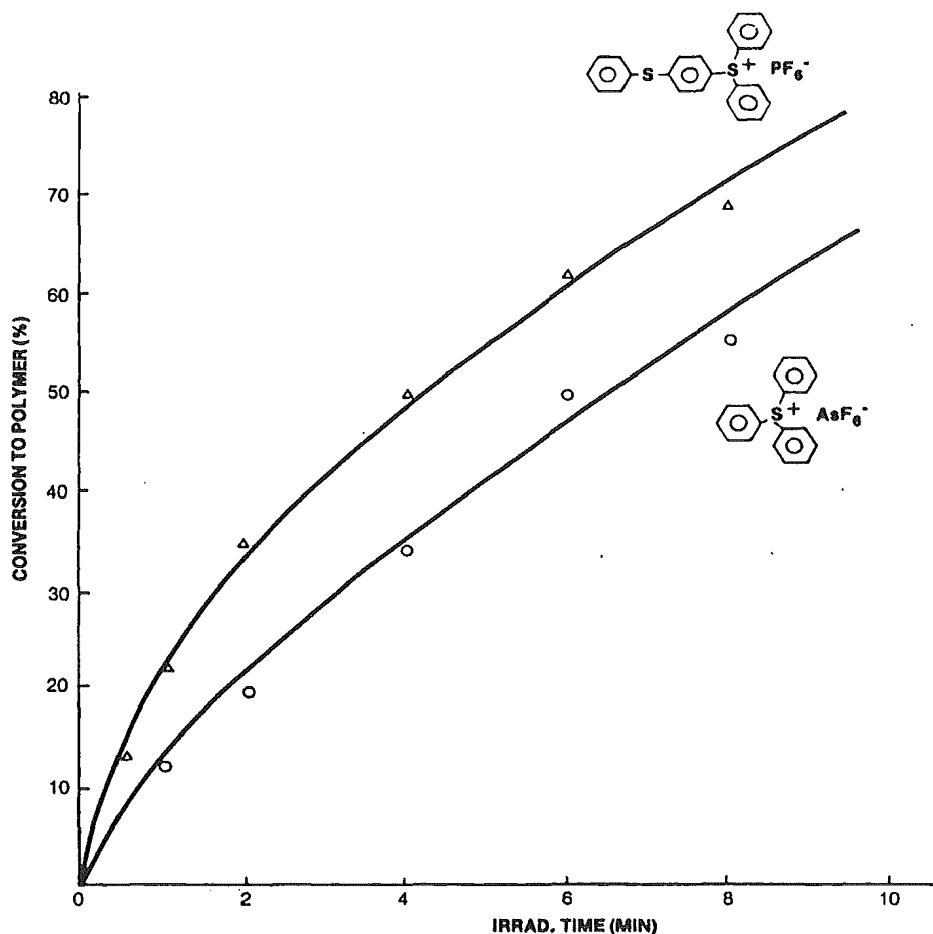
Fig. 6. Comparison of diphenyl-4-thiophenoxyphenylsulfonium hexafluorophosphate (IV) with triphenylsulfonium hexafluoroarsenate (II) in the bulk photopolymerization of cyclohexene oxide at 20°C (photoinitiator concentration = 3 mole %).

sulfonium hexafluoroarsenate salts with triphenylsulfonium hexafluoroarsenate (II) in the photoinitiated cationic polymerization of cyclohexene oxide (7-oxa-bicyclo[4.1.0]heptane). At short irradiation times (<1 min), polymerization rates are from two to three times faster using the para III isomer than the parent triphenylsulfonium salt.

It has been observed in the photopolymerization of cyclohexene oxide that for a given series of triarylsulfonium salts, the hexafluoroarsenate salts give higher rates of conversion than the corresponding hexafluorophosphates.[3] The same observation may be made in the case of the diphenyl-4-thiophenoxyphenylsulfonium salts III and IV as shown in Figure 5 in which these two anions again are compared. However, when the complex hexafluorophosphate salt IV is compared to the unsubstituted hexafluoroarsenate II in the photopolymerization
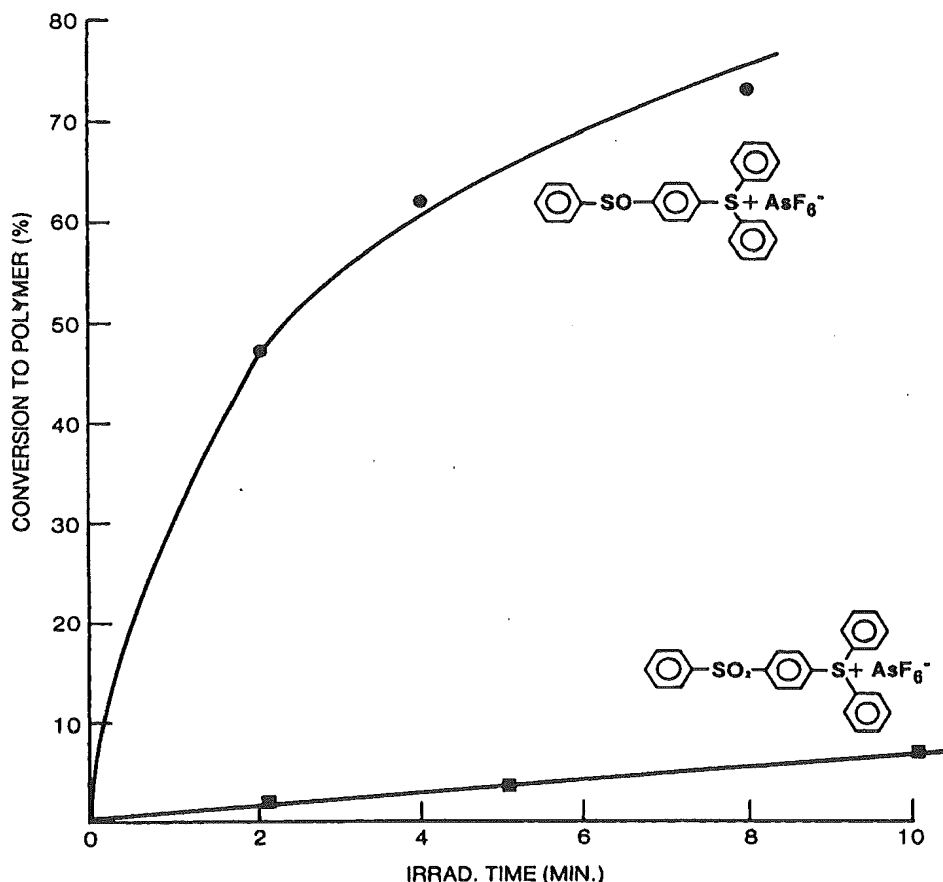
Fig. 7. Photoinitiated bulk polymerization of cyclohexene oxide at 20°C using 3 mole % IX and X.

of cyclohexene oxide (Fig. 6), the former salt is shown to give a higher rate of conversion to polymer due to its much faster rate of photolysis.

The introduction of simple alkyl substituents onto the phenyl rings of complex triarylsulfonium salts (as, for example, in salts VII and VIII) does not markedly affect the position or intensity of their ultraviolet (UV) absorption bands compared to the unsubstituted compound III. As a result, VII and VIII are as efficient as III in photoinitiated cationic polymerization. In contrast, oxidation of the sulfur atom of the thiophenoxy group of III to give sulfone X dramatically shifts the λ_{max} to shorter wavelengths (from 300 to 243 nm). The corresponding sulfoxide, IX, has UV bands which closely resemble those of its precursor salt, III. Similar differences occur in the spectra of the related compounds, diphenylsulfide [λ_{max} = 231(3.8), 250(4.08), 273.4(3.75)], diphenylsulfoxide [λ_{max} = 233(4.15), 265(3.32)], and diphenylsulfone [λ_{max} = 236.3 (4.17)],[8] which suggests that the conjugative interaction of the two aromatic rings depends on the presence of at least one lone pair of electrons on sulfur. Diphenylsulfone, in which both sulfur lone pairs are involved in coordinate covalent bonds to
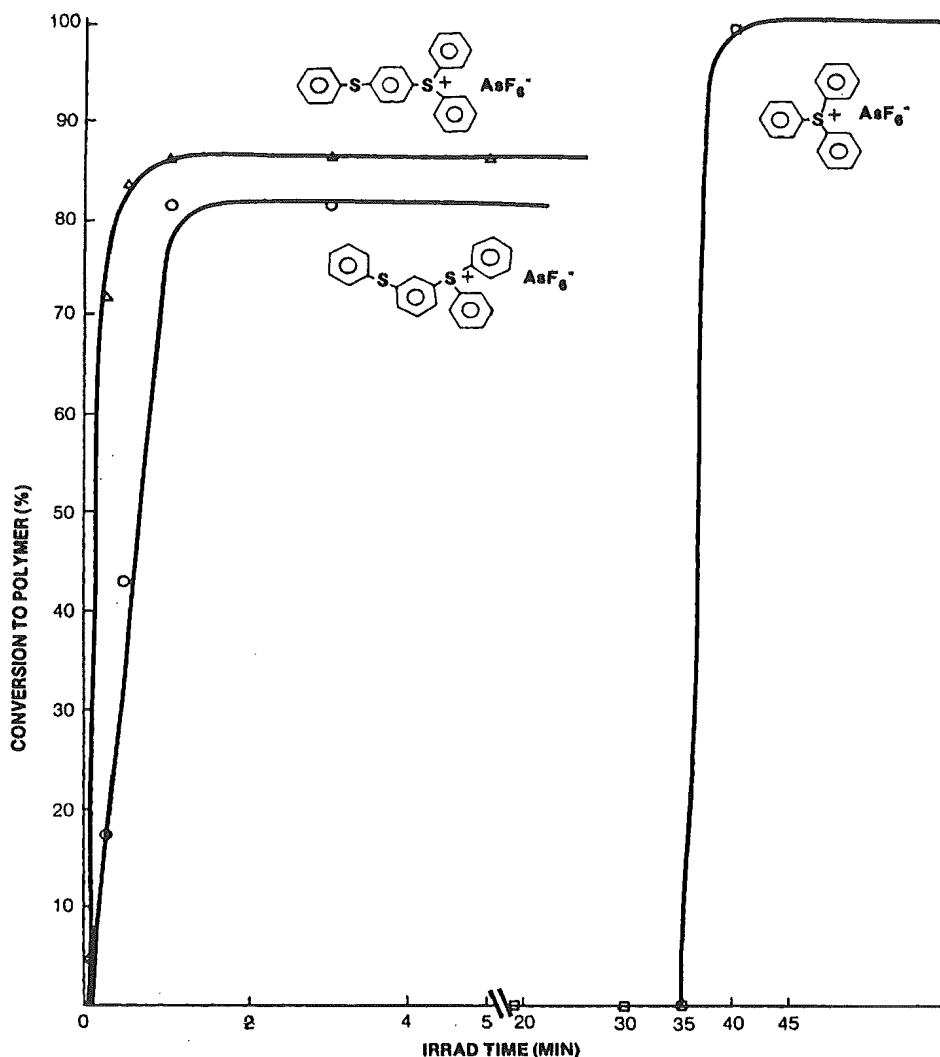
Fig. 8. Photoinitiated polymerization of 2-chloroethyl vinyl ether at 23°C in CH_2Cl_2 (0.123 × 10^{-3} mole photoinitiator, 0.123 mole 2-chloroethyl vinyl ether).

oxygen, has a typical unconjugated benzenoid spectrum. Conversely, diphenylsulfoxide and diphenylsulfide have longer-wavelength-absorbing chromophores resulting from the presence of, respectively, one and two sets of lone pairs of electrons.

The differences in the spectra of IX and X are reflected further in their relative abilities to initiate the cationic polymerization of cyclohexene oxide as shown in Figure 7. Whereas the sulfoxide IX is approximately as active as the precursor sulfide III, the sulfone has greatly reduced activity.

Cationically polymerizable monomers, other than epoxides, also are readily polymerized by diphenyl thiophenoxyphenylsulfonium salts. A comparison
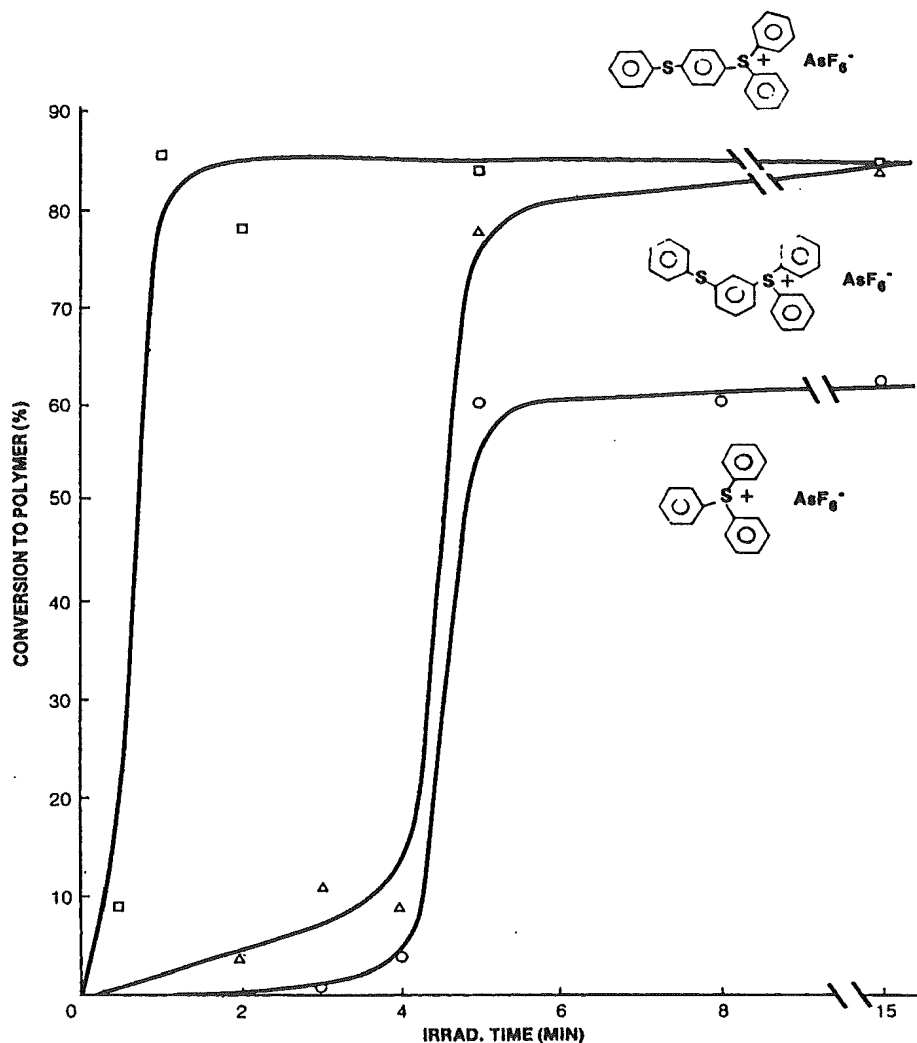
Fig. 9. Photoinitiated polymerization of s-trioxane at 21°C in CH_2Cl_2 using various photoinitiators (0.139 × 10^{-3} mole photoinitiator, 0.139 mole s-trioxane).

of the photoinitiated polymerizations of 2-chloroethyl vinyl ether by triphenylsulfonium hexafluoroarsenate II and by complex triarylsulfonium salts III and V are shown in Figure 8. Even at the very low initiator concentrations used in this study, polymerization begins immediately when the complex triarylsulfonium salts are used. In contrast, the unsubstituted salt II had to be irradiated for 38 min before significant polymerization could be observed.

Similar behavior was noted in a study of the photopolymerization of s-trioxane. The result of this study can be seen in Figure 9. In this case, not only were more rapid polymerizations achieved using the complex sulfonium salt III, but also the polymerization appears to proceed to higher monomer conversions.
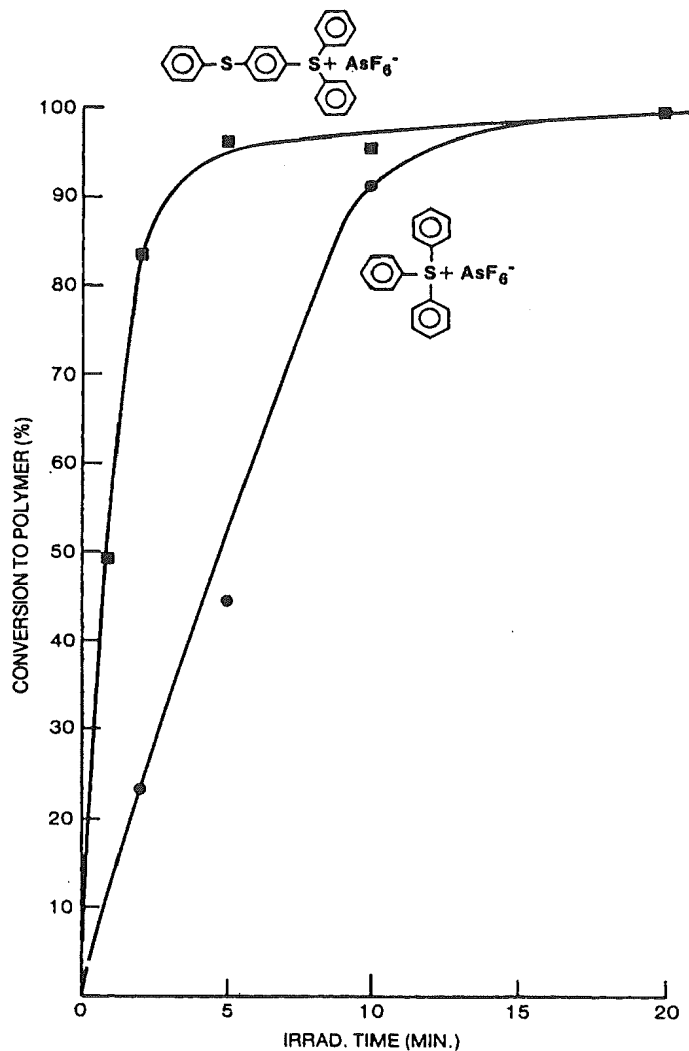
Fig. 10. Photoinitiated polymerization of β-pinene in CH_2Cl_2 at 25°C (0.126 × 10^{-3} mole photoinitiator, 0.126 mole β-pinene in 3 ml of CH_2Cl_2).

The photoinitiated cationic polymerization of β-pinene proceeds very rapidly and exothermically in the presence of triarylsulfonium salt photoinitiators. In Figure 10, the polymerization rates of this monomer using equimolar amounts of triarylsulfonium salts II and III are compared. Again, the rates of conversion to polymer are much higher in the case of the complex sulfonium salt III than with II. Intrinsic viscosities determined for the polymers in CHCl$_3$ obtained after 20 min of irradiation (99% conversion) were 0.06 and 0.08 dl/g, respectively, indicating rather low molecular weights.
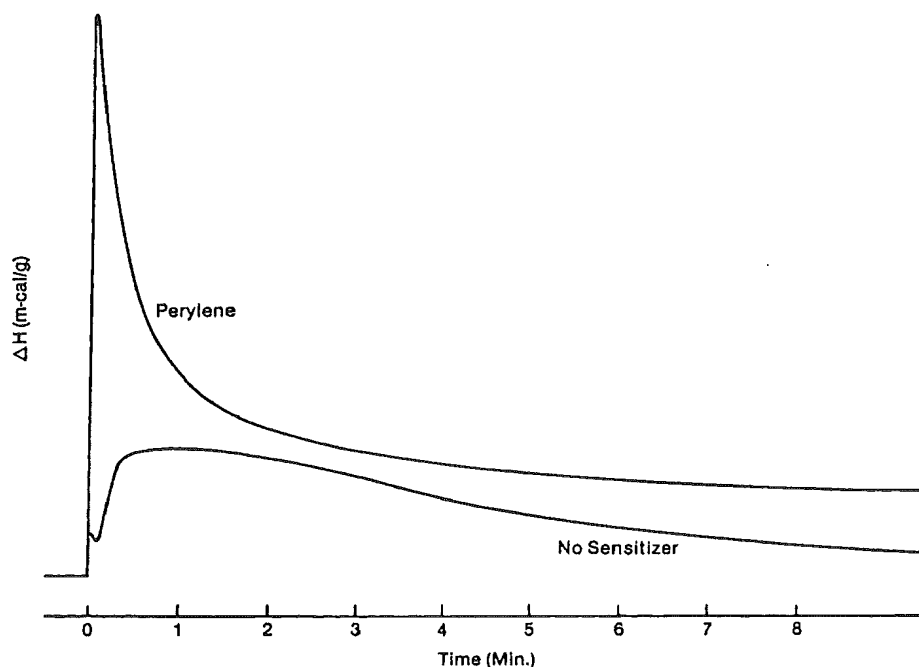
Fig. 11. DSC study of the (0.5%) perylene-sensitized photopolymerization of 3,4-epoxycyclo-hexylmethyl-3',4'-epoxycyclohexane carboxylate at 25°C using 3% complex sulfonium salt III.

Photosensitization of Complex Sulfonium Salts

The photosensitization of triarylsulfonium salts by condensed ring hydro-carbons has been reported by ourselves and others.[9,10] Success in finding suitable photosensitizers for triarylsulfonium salt photolysis has permitted the extension of the spectral sensitivity of these photoinitiators into the long-wavelength UV and to the blue region of the visible spectrum.   Complex sulfonium salts, such as diphenyl-4-thiophenoxyphenylsulfonium salts, also can be photosensitized using these same condensed ring hydrocarbons.   An example in which perylene is used to sensitize the photopolymerization of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ERL 4221) at wavelengths longer than 390 nm is shown in Figure 11.   The curves in the figure were generated with the aid of a specially equipped differential scanning calorimeter.   When no dye was present, only a slight exotherm was noted resulting from photopolymerization. This is attributed to the tail absorption of the peak at 300 nm for this sulfonium salt which extends to wavelengths greater than 390 nm.   In contrast, when perylene is added as a photosensitizer, rapid and highly exothermic polymer-ization is observed which results in a single sharp peak in the DSC curve.

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